THE ULTRAVIOLET ABSORPTION SPECTRA OF NITRIC ACID SOLUTIONS[1]

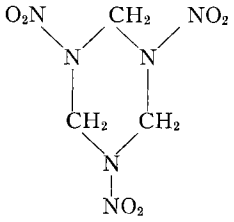
By R. Norman Jones and G. Denis Thorn

Abstract

The ultraviolet absorption spectra of binary mixtures of nitric acid, water, acetic acid, acetic anhydride, and nitrogen pentoxide have been investigated over the ranges of concentration in which the systems exhibit sufficient chemical stability. The variations in the spectra are considered in relation to the other physical properties of the systems, as reported in the literature. The ultraviolet spectrum of nitric acid in the presence both of nitrogen pentoxide and water is interpreted in terms of a series of equilibria which involve the nitrate (NO_3^-) and nitronium (NO_2^+) ions and associated and nonassociated neutral molecules. The specific gravities of anhydrous nitric acid solutions of ammonium nitrate, potassium nitrate, ammonium acetate, acetic acid at 20 ± 0.1° C. and of nitrogen pentoxide at 25 ± 0.1° C. are also reported.

Introduction

The explosive 1,3,5-trinitro-1,3,5-triazacyclohexane (I), commonly known as RDX, is manufactured by two processes. In the "Direct" process, hexamine (hexamethylenetetramine) is nitrated with a large excess of nitric



I

acid of 97.5 to 99.5% concentration by weight. In the "Combination" or "Bachmann" process a solution of hexamine in glacial acetic acid is mixed simultaneously with acetic anhydride and with a solution of ammonium nitrate in nitric acid. Considerable research has been carried out on the mechanisms of these nitration reactions. In the case of the Combination process there are reasons to believe that the reaction is one of considerable complexity, and the yields of RDX are highly sensitive to small variations in the conditions of the reaction and the composition of the reaction mixture. In the simpler Direct process the yields also vary considerably with the strength of the nitric acid.

In an attempt to gain information about the mechanism of nitration of hexamine under the conditions operative both in the Direct and Combination

[1] *Manuscript received January 18, 1949.*

Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada, and the Department of Chemistry, Queen's University, Kingston, Ontario. Issued as N.R.C. No. 1939. This paper is based on a series of reports submitted to the Associate Committee on Explosives of the National Research Council between November 30, 1942 and April 15, 1945. The manuscript was cleared for publication on April 24, 1948.

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processes, an investigation has been made of the ultraviolet absorption spectra of the individual reagents concerned in these processes, and of such binary mixtures of these reagents as are sufficiently stable at room temperature to allow of their spectrographic measurement.

The systems investigated are summarized in Table I, and are considered separately in the succeeding sections of the paper. There follows a general

TABLE I

SYSTEMS EXAMINED

System	Concentration*
A. Ammonium nitrate – water	0–80% ammonium nitrate
B. Nitric acid – water	0–20% water
C. Nitric acid – ammonium nitrate	0–54% ammonium nitrate
D. Nitric acid – potassium nitrate	0–25% potassium nitrate
E. Nitric acid – ammonium acetate	0–30% ammonium acetate
F. Nitric acid – acetic acid	0–80% acetic acid
G. Nitrogen pentoxide – acetic acid	0.054 molar with respect to nitrogen pentoxide
H. Nitrogen pentoxide – acetic anhydride	4.79 molar with respect to nitrogen pentoxide
I. Nitrogen pentoxide – carbon tetrachloride	0.282 and 0.102 molar with respect to nitrogen pentoxide
J. Nitric acid – nitrogen pentoxide	0–24% nitrogen pentoxide
K. Nitric acid – acetic anhydride	0–12 and 94–100% acetic anhydride

* *Per cent composition by weight unless otherwise indicated.*

discussion, and a section devoted to a description of the experimental techniques which were developed for the measurement of the spectra of thin films of highly corrosive materials. The general conclusions have been presented in a preliminary report (31).

A. Ammonium Nitrate – Water

Although no record of the ultraviolet absorption spectrum of aqueous solutions of ammonium nitrate has been found in the literature, the absorption is similar to that of solutions of the nitrates of the alkali metals. Hartley (25, 26) in 1902 measured the absorption spectra of aqueous solutions of several metallic nitrate salts, and observed a broad band in the region of 3020 Å; the position and intensity of this band varied only slightly with change in the cation, and he attributed it to the nitrate ion. In 1909, Baly, Burke, and Marsden (1) determined the spectra of alcoholic solutions of various nitrates and of nitric acid, and confirmed Hartley's observation that the band near 3020 Å is caused by the nitrate ion. Schaefer (41, 42) in 1915 observed that alkyl nitrate esters, unlike the nitrate salts, did not exhibit the 3020 Å absorption band; their spectra showed only "end absorption" with

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no maxima detectable in the measured region of the spectrum (compare Fig. 1). Scheibe (44), Hantzsch (22) and von Halban and Eisenbrand (16, 17, 19) have measured the absorption spectra of sodium and potassium nitrates in the presence of various salt solutions, and have noted that the

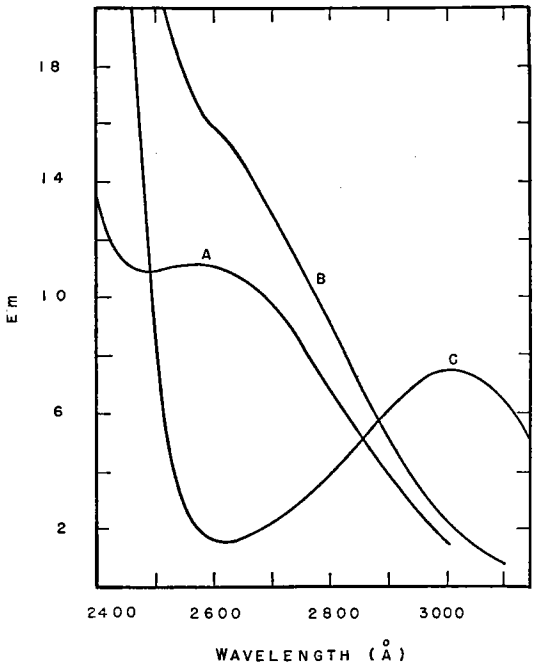

FIG. 1. *Ultraviolet absorption spectra.*
Curve A. Anhydrous nitric acid.
Curve B. Ethyl nitrate.
Curve C. Aqueous solution of ammonium nitrate.

molar extinction coefficient of the nitrate ion maximum at 3020 Å falls in intensity with increase in the concentration of the secondary electrolyte, while a new maximum appears at shorter wave lengths. Hantzsch (22) attributed these changes to solvation effects.

Experimental Observations

In these laboratories the absorption spectra of aqueous solutions containing from 0.99 to 805.4 gm. of ammonium nitrate per liter of solution have been measured. Over this concentration range the position of the maximum remains constant at 3015 Å (Fig. 1. Curve *C*); the molecular extinction coefficient at the maximum ($E_{m_{max}}$) changes only slightly, falling from 7.6 for dilute solutions to 6.9 for the most concentrated solution (see Table II). This absorption maximum can, without doubt, be attributed to the nitrate ion, and it may be inferred from the data in Table II that aqueous solutions of ammonium nitrate undergo little change in ionic condition as the concentration increases.

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TABLE II

ABSORPTION OF AQUEOUS AMMONIUM NITRATE. INTENSITY AT THE MAXIMUM

Concentration, gm./liter	$\log \frac{I_0}{I}$	Depth of solution, mm.	E_m at 3015 Å
0.99	0.094	10.00	7.5
2.99	0.279		7.5
3.32	0.316		7.6
4.67	0.433		7.4
5.53	0.517		7.5
10.83	0.107	1.06	7.4
20.01	0.196		7.5
30.30	0.306		7.6
40.07	0.397		7.5
	0.043	0.114	7.5
100.81	0.116		7.4
150.2	0.156		7.3
250.9	0.251		7.0
276.1	0.275		7.0
330.9	0.330		6.9
396.7	0.395		7.0
517.1	0.524		7.1
	0.090	0.0196	7.1
805.4	0.136		6.9

B. Nitric Acid – Water

The ultraviolet absorption spectrum of nitric acid has received extensive study from several investigators. The spectra of dilute solutions of nitric acid are similar to those of the alkali nitrates (1, 17, 18, 19, 22, 26, 33, 37, 41) but changes occur as the concentration of the nitric acid is increased. Hartley (26) noted that the nitrate ion absorption band near 3020 Å disappeared with increase in the nitric acid concentration. Schaefer (41-43) measured the absorption of aqueous solutions containing up to 98.6% of nitric acid by weight, and found no maxima for concentrations greater than 63% (14 *N*): his data indicate that 92% acid (22 *N*) exhibits a higher intensity near 2600 Å than 99% acid (23.7 *N*) (*vide infra*). The absorption of 0.2 *N* potassium nitrate dissolved in sulphuric acid of increasing concentration was similar to that of increasing concentrations of nitric acid in water. Von Halban and Eisenbrand (19) investigated the absorption of nitric acid at concentrations up to 68% (15.3 *N*) and noted the decrease in the intensity of the nitrate ion band with increasing concentration. They also observed a maximum at 2650 Å in the spectrum of solutions of nitric acid in anhydrous ether and attributed this band to the presence of unionized $HO-NO_2$ molecules. Hantzsch (21, 22) found no maximum in the absorption curve of 100% nitric acid, nor in the curve of a solution of nitric acid in anhydrous ether; he did note that a band appeared on addition of a trace of water to such an ethereal solution. Hantzsch discusses both his own work and that of Von Halban and Eisenbrand in a long critical paper (22) in which he explains the effects of dilution on the spectrum of nitric acid in terms of a complex series of equilibria involving a hydrolysis of "nitracidium nitrate" $\{[ON(OH)_2]^+ NO_3^-\}$

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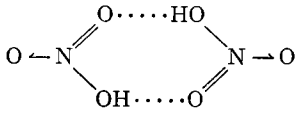
to a "pseudoacid" (O_2N-OH) followed by hydration of the pseudo acid and, on further addition of water, its conversion to "hydroxonium nitrate" [$(NO_3)H_3O$] which then ionizes.

Although, as will be apparent later, the changes which occur on the increasing addition of water to anhydrous nitric acid must involve a series of equilibria comparable in complexity with those postulated by Hantzsch, most of this earlier spectrometric work would seem to be reconcilable with a simple ionic equilibrium between unionized nitric acid molecules ($HO-NO_2$) with an absorption maximum at 2600 to 2650 Å and a nitrate ion with a weaker absorption maximum at 3015 to 3020 Å, viz.,

$$HO\text{-}NO_2 + H_2O \rightleftharpoons NO_3^- + H_3O^+$$

Except for some measurements by Dalmon and Bellin (11, 12) and by Kortüm (33), little work appears to have been done recently on the ultraviolet absorption of concentrated solutions of nitric acid, but it is relevant to consider some measurements on other physical properties. The *refractive indices* of aqueous solutions of nitric acid when plotted against the per cent composition give a linear relation over the range from 78 to 91%. At 91% a sharp inflection occurs, and above 98.5% the slope of the line is reversed (48). The *electrical conductivity* also behaves abnormally over this concentration range, as was observed by Veley and Manley (48) and confirmed recently in these laboratories by Taylor (31).

Several investigators have examined the *infrared* and *Raman spectra* of aqueous solutions of nitric acid. Dalmon and Freyman (13) have recorded the very near infrared spectrum of 80 to 100% nitric acid, and have noted an absorption band at 1.017 μ in the spectrum of the anhydrous acid, which they attributed to the associated molecule II. On the progressive addition of water this band diminishes in intensity and a new band develops at 0.97 μ.



II

At a concentration of 80% the 1.017 μ band has almost disappeared. Dalmon and Freyman consider that the 0.97 μ band may be due to a hydroxyl group. These observations confirm earlier work of Kinsey and Ellis (32). A theoretical treatment of the infrared absorption spectrum of nitric acid has recently been attempted by Bauer and Magat (2), the results of which are claimed to be in accordance with the observations of Dalmon and Freyman.

Nitric acid below 30% gives a *Raman spectrum* similar to that of the alkali nitrates and differing from the spectrum of the concentrated acid (3, 7-9, 15, 35, 36, 38-40, 45).

When the concentration is increased above 30% new Raman lines appear. In the spectrum of the anhydrous acid no lines attributable to the nitrate ion

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are observed; two faint lines ($\Delta\ \nu$ 1050 $cm.^{-1}$ and 1400 $cm.^{-1}$) in the spectrum of anhydrous nitric acid were attributed by Chédin to nitrogen pentoxide, which he estimates may be present in anhydrous nitric acid to the extent of about 1%. Chédin observed that these weak bands can still be seen in acid of 99.6% concentration. Most of the studies on the Raman spectrum of nitric acid have been qualitative only, and no systematic studies over the range from 80 to 100% at small increments in concentration appear to have been made. This subject has been reviewed by Hibben (28).

Recently Bennett, Brand, and Williams (4, 5) have put forward evidence indicating that solutions of nitric acid in sulphuric acid may contain molecular species other than $HONO_2$ and NO_3^-, and they attribute the Raman line at 1400 $cm.^{-1}$ to the nitronium (NO_2^+) ion.

These abnormalities in the physical constants of concentrated nitric acid solutions are of particular interest in relation to the marked influence of acid concentration on the yields of RDX obtained in the nitration of hexamine. They suggest that some species of molecule or ion may be present in maximal concentration in nitric acid containing a small but significant amount of water, a molecule or ion which may be the primary agent in the nitration process.

Experimental Observations

The ultraviolet absorption spectra of aqueous solutions of nitric acid have been determined over the concentration range from 80 to 100% nitric acid. A maximum occurs at 2565 Å in the spectrum of the anhydrous acid with $E_{m_{max}}$ 11.1. The position of the maximum shifts to 2615 Å as the concentration falls to 95% and remains unchanged with further dilution to 90%. With diminishing concentration the molecular extinction coefficient at the maximum decreases to 9.5 for 95% acid, increases again to 11.5 for an acid of 92% strength, and then falls slowly on further dilution. These changes are shown in the series of curves in Fig. 2. In Fig. 3 the value of $E_{m_{max}}$ is plotted against the acid concentration. In Table III the wave lengths and the intensities at the maxima are listed for all the nitric acid samples studied. The value of $E_{m_{max}}$ in the last column is an averaged value of two or more spectrographic measurements on the same acid sample. The reproducibility of $E_{m_{max}}$ on a series of determinations on the same sample of diluted acid was about 2%. However, the values obtained for $E_{m_{max}}$ on different preparations of acid diluted to approximately the same concentration varied in some cases by several per cent. These variations are responsible for the scatter of the points in Fig. 3. They are caused most probably by uncertainties in the determination of the acid concentration (see Experimental Section, page 602).

C. Nitric Acid – Ammonium Nitrate

It does not seem that the ultraviolet absorption spectrum of ammonium nitrate dissolved in anhydrous nitric acid has been determined previously, but Médard and Petitpas (35, 36) have examined the Raman spectra of such

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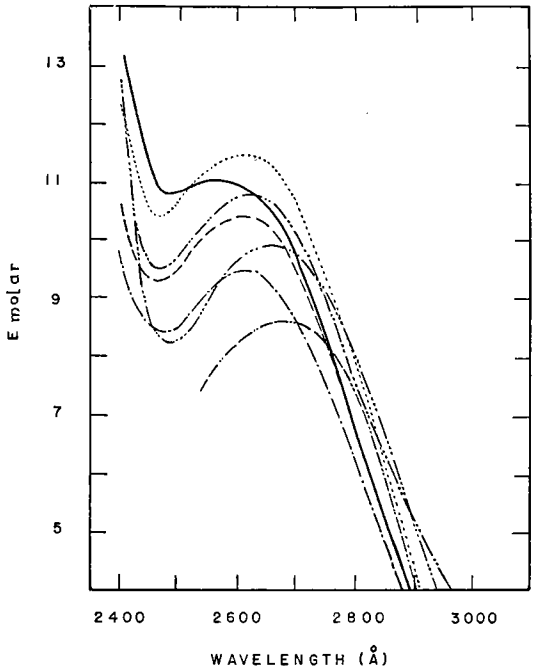

FIG. 2. *Ultraviolet absorption spectra of aqueous nitric acid:—*

————	100.0% HNO_3	–··–··–·–	90.0% HNO_3
– – – – –	97.0%	–···–···–···	80.1%
–·–·–·–·–	95.0%	––··––·–––··	68.6%*
·····	92.2%		

(*) Taken from data of von Halban and Eisenbrand (reference 19).

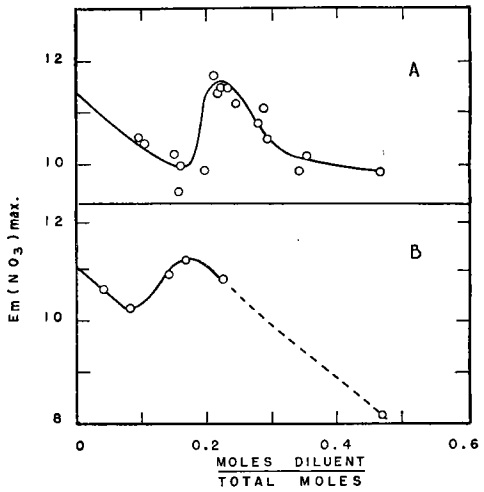

FIG. 3. *Variation of the molecular extinction coefficient at the maximum for nitric acid. A. Dilution with water; B. Dilution with ammonium nitrate.*

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TABLE III

ABSORPTION SPECTRUM OF 80 TO 100% NITRIC ACID. POSITION AND INTENSITY OF THE MAXIMUM

Concentration		Wave length of maximum, Å	E_{mmax} (individual measurements on the same acid sample)	E_{mmax} (average)
% Nitric acid	Mole fraction of water			
100.0	0.000	2565	11.15, 11.30 11.10, 11.01 10.90	11.1
97.2	0.092	2600	10.40, 10.40, 10.80	10.5
96.9	0.101	2610	10.70, 10.55, 10.15	10.4
95.3	0.147	2610	10.40, 10.52, 9.90, 10.20	10.2
95.0	0.155	2610	9.54, 9.54	9.5
94.9	0.158	2610	9.92, 10.02	10.0
93.6	0.193	2615	9.84, 9.93	9.9
93.0	0.208	2610	11.68, 11.80	11.7
92.7	0.213	2615	11.43, 11.43	11.4
92.6	0.218	2610	11.80, 11.40, 11.40	11.5
92.2	0.228	2610	11.50, 11.48	11.5
91.7	0.240	2615	11.20	11.2
90.1	0.277	2615	10.80, 10.82	10.8
89.9	0.282	2615	11.10, 11.10	11.1
89.5	0.291	2625	10.60, 10.35	10.5
87.2	0.339	2635	9.90, 9.95	9.9
83.4	0.409	2650	10.30, 10.30, 10.15	10.2
80.1	0.465	2650	9.88, 10.00	9.9

solutions. They note that, on the addition of the salt, shifts occur in the positions of the Raman lines similar to those produced by the addition of small amounts of water.

Experimental Observations

The ultraviolet absorption spectra have been measured of solutions containing up to 54 gm. of ammonium nitrate in 100 gm. of solution.* The results are recorded in Table IV and in Fig. 4.

The effect of addition of ammonium nitrate on the ultraviolet absorption spectrum of anhydrous nitric acid parallels the effects noted by Médard on the Raman spectrum. Small additions cause a fall in the intensity of the absorption maximum near 2625 Å. Further addition of ammonium nitrate causes the intensity of $E_{m_{max}}$ to increase and at higher concentrations it again falls. These variations are plotted against the concentration in Fig. 3. The considerable shift of the wave length of the absorption maximum in the mixture containing 54% ammonium nitrate is probably caused in part by the additive effect of the nitrate ion absorption maximum at 3015 Å contributed by the anion of the added salt.

* *At the temperature at which these spectra were measured (approximately 20° C.) a two phase system occurs for nitric acid – ammonium nitrate mixtures over the concentration range between 27 and 52% of ammonium nitrate by weight. A single phase is obtained between 52 and 57% and below 27% ammonium nitrate.*

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TABLE IV

ABSORPTION SPECTRUM OF NITRIC ACID – AMMONIUM NITRATE. POSITION AND INTENSITY OF THE MAXIMUM

Concentration		Wave length of maximum, Å	E_{max} (NO_3)*
% NH_4NO_3	Mole fraction NH_4NO_3		
0.0	0.000	2565	11.1
5.0	0.040	2615	10.6
10.0	0.080	2625	10.3
17.0	0.139	2635	10.9
20.0	0.165	2650	11.2
26.8	0.224	2665	10.8
54.0	0.470	2775	8.2

* *See page 598.*

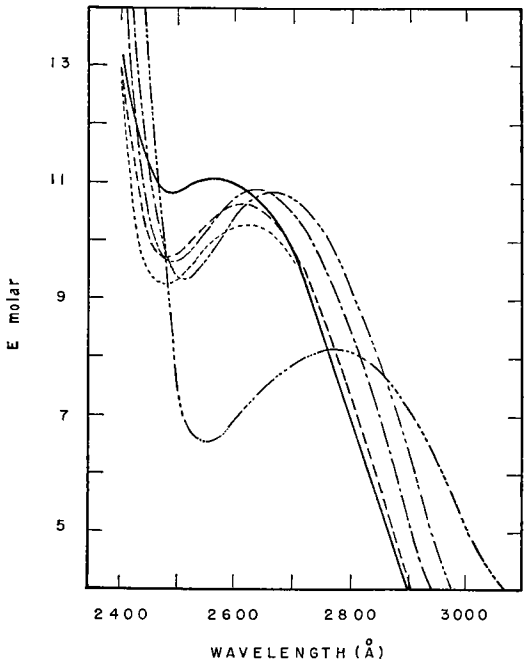

FIG. 4. *Ultraviolet absorption spectra of nitric acid – ammonium nitrate mixtures.*

———— 100.0% HNO_3 —·—·—·—· 17.0% NH_4NO_3
– – – – – – 5.0% NH_4NO_3 —··—··—·· 26.8% "
····· 10.0% " —···—··— 54.0% "

D. Nitric Acid – Potassium Nitrate

Experimental Observations

The ultraviolet absorption spectra of solutions containing up to 25% of potassium nitrate in anhydrous nitric acid are shown in Fig. 5, and the

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variation of E_{max} is plotted in terms of the mole fraction of potassium nitrate in Curve *A* of Fig. 8.

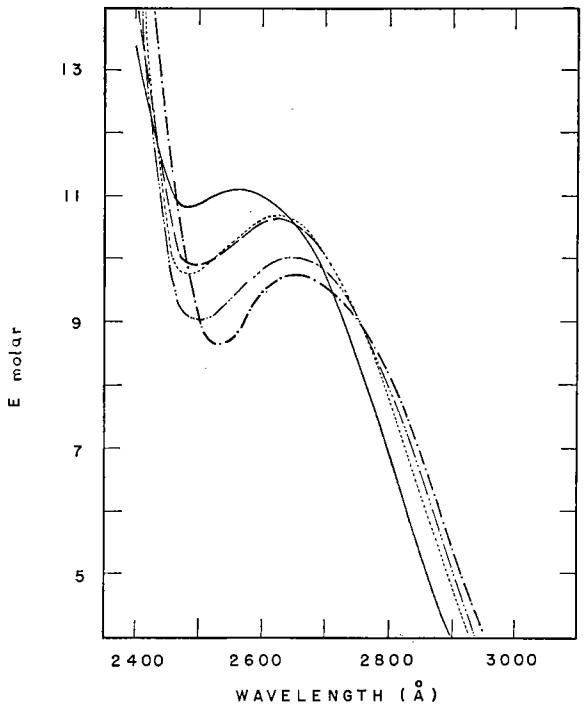

FIG. 5. *Ultraviolet absorption spectra of nitric acid – potassium nitrate mixtures.*

——————— 100.0% HNO_3 —·—·—·— 20.0% KNO_3
– – – – – – 10.0% KNO_3 —·—·—·— 25.0% KNO_3
····· 15.0% KNO_3

There is a suggestion that E_{max} does not diminish steadily, and an inflexion may be present in the neighborhood of 0.1 mole potassium nitrate. A similarity to the behavior of the nitric acid–ammonium nitrate system is indicated but the data are insufficient to establish this with certainty.

E. Nitric Acid – Ammonium Acetate

Experimental Observations

The spectra of solutions containing up to 30% of ammonium acetate in anhydrous nitric acid are recorded in Fig. 6. As with the other binary systems of salts with nitric acid, there is a suggestion of a fall and subsequent rise to a maximum in the curve of $E_{m_{max}}$ plotted against increasing concentration of the added salt (Fig. 8).

During the manipulation of these solutions the odor of acetic acid seemed to increase as the concentration of the ammonium acetate became larger.

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In order to determine whether acetic acid was being produced in accordance with the equilibrium:

$$CH_3 . COO^- + NH_4^+ + HNO_3 \rightleftharpoons NH_4^+ + NO_3^- + CH_3 . CO . OH$$

a ternary solution of ammonium nitrate, nitric acid, and glacial acetic acid was prepared; the molecular proportions of the three constituents were

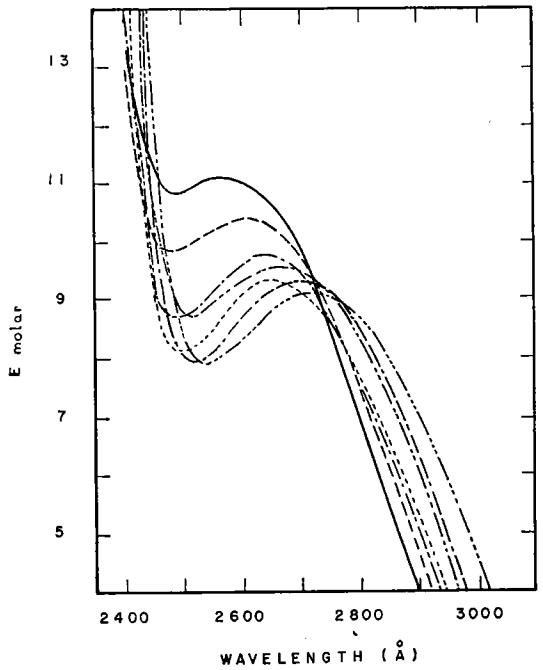

FIG. 6. *Ultraviolet absorption spectra of nitric acid – ammonium acetate mixtures.*

————	100.0% HNO_3	–·–·–·–	20.6% NH_4OAc.
– – – – –	5.0% NH_4OAc.	–··–··–··	25.0% "
–·–·–·–·–	9.8% "	–···–···–···	29.9% "
·····	15.0% "		

adjusted to yield the same molar proportions* as in the most concentrated of the ammonium acetate – nitric acid solutions shown in Fig. 6. Both the densities and the absorption spectra of these two solutions were the same. Taylor (46) has investigated the electrical conductivity of mixtures of nitric acid, acetic acid, and ammonium acetate, and has observed that solutions of identical conductivity can be prepared by mixing either ammonium acetate and nitric acid or ammonium nitrate and acetic acid in suitable proportions.

**For the curve indicated as —···—···—··· the mole fraction of ammonium acetate was 0.259. This ternary solution was made up to have a mole fraction of acetic acid of 0.258, ammonium nitrate 0.258, and nitric acid 0.484. The molecular extinction coefficient at the maximum calculated for nitric acid was 9.0, and can be compared with 9.1 for the ammonium acetate – nitric acid solution.*

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F. Nitric Acid – Acetic Acid

Viscosity and freezing point measurements suggest that compound formation may occur between these two acids, but the Raman spectra of such mixtures exhibit the characteristic frequencies of each component without the appearance of any new lines (6).

Experimental Observations

The ultraviolet absorption spectra of solutions containing up to 50% of anhydrous acetic acid in anhydrous nitric acid are shown in Fig. 7. When

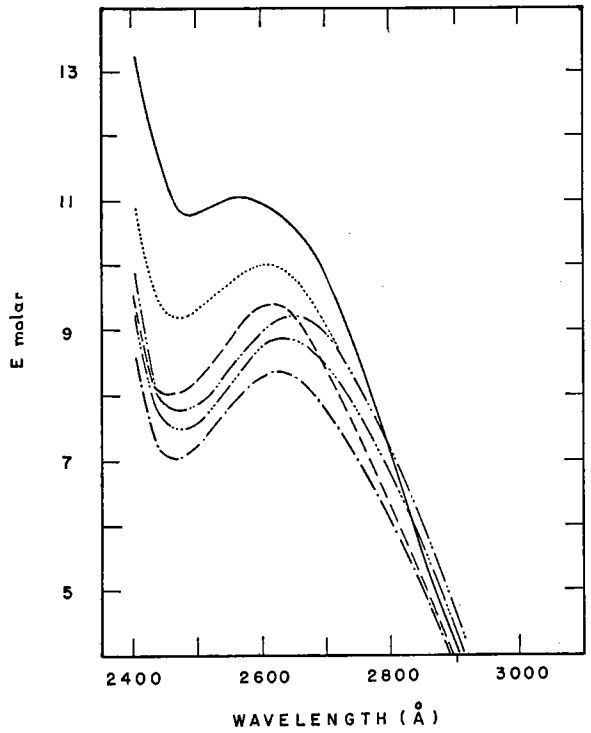

FIG. 7. *Ultraviolet absorption spectra of nitric acid – acetic acid mixtures.*

————	100.0% HNO_3	–·–·–·–	30.6% HOAc.
·····	7.0% HOAc.	–···–··–	39.0% "
– – – – – –	12.3% "	–·–··–··	49.4% "

the intensity at the maximum is plotted against the composition of the solution, the same type of curve is obtained as with the other binary systems containing nitric acid (Fig. 8).

G, H, I. Nitrogen Pentoxide

The changes in the absorption spectrum of anhydrous nitric acid brought about by the addition of small quantities of water or other solutes might arise

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from the effects of the solute on an equilibrium, in "anhydrous nitric acid," between nitric acid, water, and nitrogen pentoxide, viz.:—

$$2HNO_3 \rightleftharpoons H_2O + N_2O_5$$

This consideration prompted the extension of these investigations to include systems containing nitrogen pentoxide.

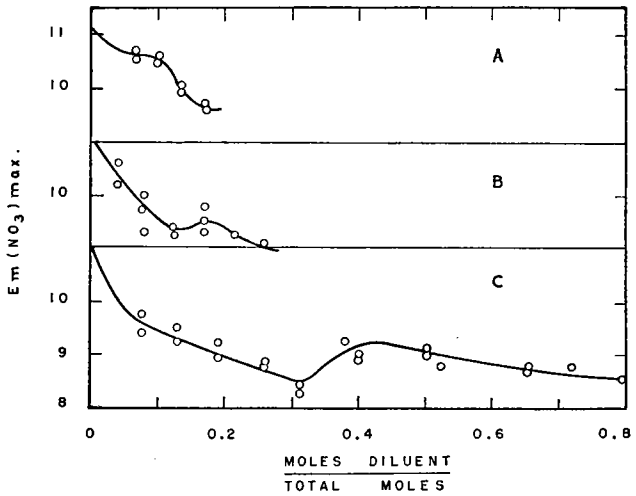

FIG. 8. *Variation of the molecular extinction coefficient at the maximum for nitric acid.*
A. Dilution with potassium nitrate.
B. Dilution with ammonium acetate.
C. Dilution with acetic acid.

Experimental Observations

The spectra of nitrogen pentoxide in acetic acid, acetic anhydride, and in carbon tetrachloride are recorded in Fig. 9. These show no maxima, but indicate that the absorption is very intense below 2700 Å. In acetic acid the spectrum differs somewhat from that in the other solvents, there being evidence of an inflection at 2750 Å.

J. Nitric Acid – Nitrogen Pentoxide

Experimental Observations

The spectra of solutions of anhydrous nitric acid containing up to 24% by weight of nitrogen pentoxide are recorded in Fig. 10. It is seen that as the amount of nitrogen pentoxide is increased, the absorption maximum at 2615 Å soon becomes obliterated by the intense absorption of the added solute.

K. Nitric Acid – Acetic Anhydride

Experimental Observations

The range of concentration over which this system can be investigated is limited, since, at room temperature, mixtures containing from 12% to 94% of

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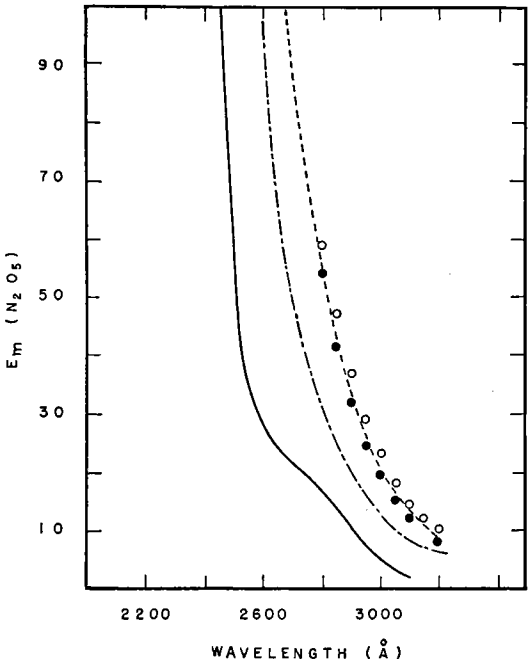

FIG. 9. *Ultraviolet absorption spectrum of nitrogen pentoxide in various solvents.*
——— *0.054 molar solution in acetic acid.*
-·-·-·- *4.79 molar solution in acetic anhydride.*
– – – – – – – – *0.282 molar solution in carbon tetrachloride.*
" ○ ○ ○ *0.102 molar solution in carbon tetrachloride.*

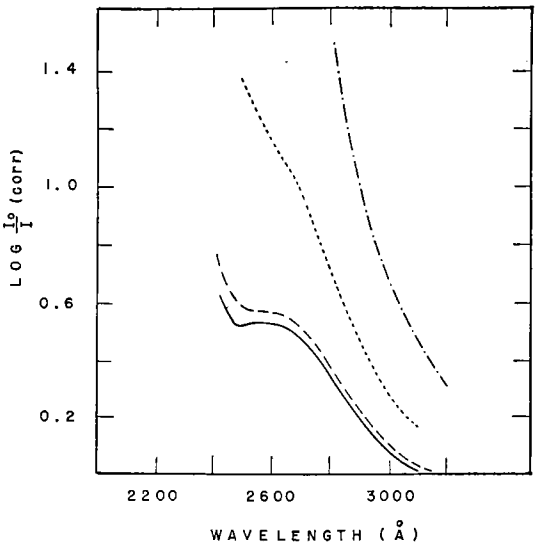

FIG. 10. *Ultraviolet absorption spectra of nitric acid – nitrogen pentoxide mixtures (optical density corrected for change in the specific gravity of the solution. See page 598).*
——— 100% HNO_3 ····· 12% N_2O_5
– – – – 3% N_2O_5 -·-·-·- 24% N_2O_5
(Cell thickness 0.0196 mm.)

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acetic anhydride are unstable and are liable to undergo spontaneous decomposition. The spectra of mixtures outside of this unstable range which were examined are shown in Fig. 11. These curves exhibit significant similarities

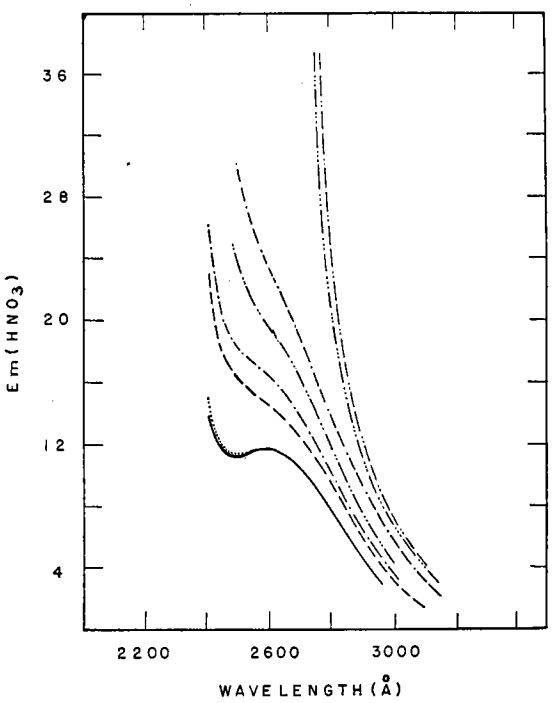

FIG. 11. *Ultraviolet absorption spectra of nitric acid – acetic anhydride mixtures.*

————	1.26% Ac_2O	– – – – – –	12.16% Ac_2O
.....	3.19% "	–.–.–.–	94.72% "
– – – – –	6.74% "	–..–..–	96.84% "
–.–.–.–.–	7.24% "		
–..–..–..	9.46% "		

to the curves for the nitric acid – nitrogen pentoxide system shown in Fig. 10. At high concentrations of acetic anhydride the curves resemble those of high concentrations of nitrogen pentoxide in nitric acid, and at low concentrations of acetic anhydride they resemble the solutions of low concentrations of nitrogen pentoxide in nitric acid. Since acetic anhydride is nonabsorbent in this region of the spectrum (24, 34), these observations suggest the existence of an equilibrium:—

$$(CH_3CO)_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2CH_3COOH$$

in which the equilibrium position lies well to the right-hand side.

Discussion

A comparison of the absorption spectra of nitric acid solutions containing small amounts of water (Fig. 2) with the spectra of nitric acid solutions

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containing small amounts of nitrogen pentoxide (Fig. 10) suggests that the latter group of curves manifest a continuation of a series of changes which commences with the 95% acid and passes smoothly through the anhydrous acid to the acids containing excess nitrogen pentoxide.*

With this in mind, the changes in the spectra of aqueous nitric acid which occur over the concentration range from 80 to 100% may be described in the following terms. Between 80 and 95% a molecular species predominates which is responsible for the absorption maximum near 2600 Å. This molecule or ion, which may be designated the "2600 Å chromogen" is present in maximal concentration at 91 to 92%. At 95 to 96%, changes occur in the spectrum which can be attributed to the presence of "free nitrogen pentoxide" in the solution.

In Table V the *persistence* of the 2600 Å band is listed for various concentrations; the persistence is defined as the ratio of the molecular extinction coefficient at the maximum near 2600 Å to that at the minimum near 2500 Å. The persistence constitutes a convenient numerical index of the prominence of the absorption band, and its continuous diminution with increasing nitric acid concentration indicates that the curve is progressively flattening. This effect is superimposed on the rise of E_{2600} to a maximum at 91 to 92%.

It would seem necessary to invoke two variables to explain these changes, (*a*) an increase in the concentration of the 2600 Å chromogen between 80 and 92% and (*b*) the appearance of a new molecular or ionic species exhibiting intense structureless absorption, which we have tentatively identified above as "free nitrogen pentoxide."

Examination of the persistence values in Table V shows furthermore that between 97 and 100% the rate of fall is greater than at lower nitric acid concentrations, indicating that small decreases in water content produce progressively greater increases in the "free nitrogen pentoxide" concentration as the anhydrous condition is approached.†

Between 93 and 96% the absolute intensity of the maximum falls off. In view of the very great intensity of the nitrogen pentoxide absorption, the concentrations of this substance required to produce the observed flattening

* *Hantzsch (22) has questioned the claim of von Halban and Eisenbrand (19) that an ethereal solution of anhydrous nitric acid possesses an absorption maximum at 2650 Å; he reported that no such maximum is present if the ether is truly anhydrous, a maximum appearing only on the addition of a drop of water to the solution. Hantzsch also failed to observe any maximum in the absorption spectrum of anhydrous nitric acid. One would infer from Hantzsch's paper that the maximum observed by von Halban and Eisenbrand resulted from the use of moist ether. Hantzsch's failure to detect the maximum in the spectrum of nitric acid, either in the free state or in ethereal solution, might very well be caused by his using anhydrous nitric acid containing appreciable quantities of dissolved nitrogen pentoxide.*

† *One of the referees has commented on our use of the persistence concept and has suggested that we try to use the E values to calculate the percentage of nitrogen pentoxide present at various concentrations. This had been considered previously, but the idea was discarded since the molecule or ion actually contributing to the absorption which we attribute to "free nitrogen pentoxide" is almost certainly a constituent of an equilibrium mixture and its absorption is very unlikely to obey a Beer's law relation based on the nitrogen pentoxide curves in Fig. 9. A strict mathematical treatment of the curves seemed of doubtful significance in these circumstances. We therefore used the persistence treatment so as to be able to describe the changes of curve shape with concentration in a semiquantitative manner.*

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TABLE V

PERSISTENCE OF THE 2600 Å BAND IN NITRIC ACID – WATER

% HNO_3	E_{max}/E_{min}	% HNO_3	E_{max}/E_{min}
100	1.02	90	1.14
97	1.12	87	1.17
95	1.13	80	1.20

effect must be exceedingly small, and it would seem reasonable to surmise that in addition to the formation of free nitrogen pentoxide, other factors may be operative over this concentration range in reducing the concentration of the 2600 chromogen.

The nature of the 2600 chromogen has been discussed by earlier workers, and von Halban and Eisenbrand (19) identify it with the nonassociated $HO–NO_2$ molecule (Hantzsch's pseudoacid). This would seem to be largely a speculative hypothesis, although it is supported to some extent by the resemblance to the spectrum of the alkyl nitrate esters (Fig. 1). The effect of the addition of small amounts of water, acetic acid, or various inorganic salts in bringing about an increase in the concentration of this species is difficult to explain. If the existence of associated molecules which are non-absorbent in this region of the spectrum be postulated, the observed effects could be explained by assuming that the added solute brings about a "deassociation". This would be in line with Dalmon and Freyman's interpretation of the changes in the infrared spectrum of nitric acid on dilution with water to 80% (see page 584).

It is relevant to note here that the system nitric acid – ammonium nitrate exhibits no unusual features over the measured concentration range which would suggest specific complex formation or other abnormal type of behavior to account for its essential role in the Bachman process for the manufacture of RDX.

Nitrogen Pentoxide

The main source of information concerning the presence of nitrogen pentoxide in nitric acid is the Raman spectrum (28). It has already been noted (page 584) that in the Raman spectrum of anhydrous nitric acid a line appears at $\Delta\nu = 1400$ $cm.^{-1}$ This line is very prominent in anhydrous nitric acid containing 20% of phosphorus pentoxide, as also are two lines 1050 and 1100 $cm.^{-1}$, which are faint in the spectrum of pure anhydrous nitric acid. In the Raman spectrum of crystalline nitrogen pentoxide there are two lines at 1050 and 1400 $cm.^{-1}$ which are identical in position with those which augment in intensity on addition of nitrogen pentoxide to anhydrous nitric acid. The same lines occur also in the Raman spectra of certain nitric acid – sulphuric acid mixtures (4, 5, 9).

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These lines are not seen in the spectra of solutions of nitrogen pentoxide in carbon tetrachloride or phosphorus oxychloride, there being instead three other prominent lines near 1330, 1250, and 880 $cm.^{-1}$ The infrared spectrum of gaseous nitrogen pentoxide is very similar to that of a solution in carbon tetrachloride (10, 27). The evidence from Raman and infrared spectra thus indicates that nitrogen pentoxide exists in one form in the gaseous state and in solution in chlorinated solvents, and in a different form in the crystalline state and in solution in anhydrous nitric acid.

Bennett, Brand, and Williams (4, 5) have drawn attention to these anomalies in the Raman spectrum of anhydrous nitric acid, and in support of their contention that the Raman line at 1400 $cm.^{-1}$ in mixtures of nitric acid – sulphuric acid is caused by the NO_2^+ ion they make use of the ingenious argument that such an ion would be isosteric with carbon dioxide and might be expected to possess similar vibrational characteristics. Carbon dioxide possesses a prominent Raman line near 1400 $cm.^{-1}$ It would seem to us that this hypothesis necessitates the further conclusion that, as a line is present also at the same frequency in the Raman spectrum of nitrogen pentoxide in the crystalline state, that too contains the NO_2^+ ion, suggesting an ionic lattice structure of NO_2^+ and NO_3^- ions. If this is so, some evidence of the presence of NO_3^- might be expected to show up in the infrared spectrum of crystalline nitrogen pentoxide.*

Up to 1946 no real evidence of the presence of NO_2^+ or other nitrogen containing cation in nitric acid (in the absence of sulphuric acid) had been obtained, except possibly for Hantzsch and Berger's observation (23) that, on the electrolysis of "nitracidium perchlorate" in nitromethane solution there occurs a migration of nitrogen containing groups toward the cathode. In these laboratories Taylor, Lyne, and Follows have investigated the electrical conductivity of the system water – nitric acid – nitrogen pentoxide and shown that the equivalent conductivity is minimal for 96% acid, increases sharply as the acid approaches the anhydrous condition, and continues to increase smoothly as nitrogen pentoxide is added. This would indicate an increase in the ionic population of the solution above 96%. To explain this, Taylor suggested that nitrogen pentoxide may be undergoing ionic dissociation as shown below; such dissociation need not be extensive to explain the observed conductivity changes.

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$$

The ultraviolet absorption spectra of the water – nitric acid – nitrogen pentoxide system are readily reconcilable with this hypothesis. In such a system the weak absorption of the nitrate ion at 3020 Å may be obliterated by more intense "nitrogen pentoxide absorption". The latter might be caused by the NO_2^+ ion, or by the undissociated nitrogen pentoxide molecule.

* *A similar hypothesis concerning the structure of crystalline nitrogen pentoxide has been advanced by Ingold, Millen, and Poole (30).*

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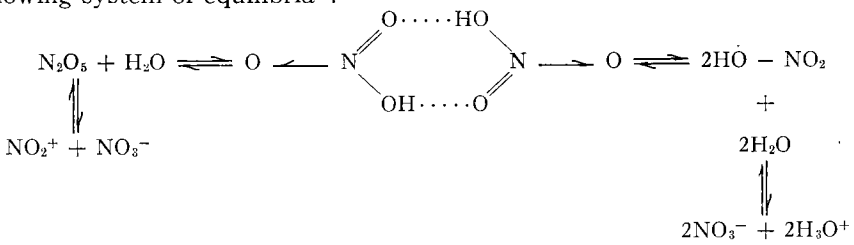
The considerations outlined in this discussion may be summarized in the following system of equilibria*:—



Experimental Technique

Most of the absorption intensity data are recorded in terms of the molecular extinction coefficient (E_m). For the case of an absorbing solute dissolved in a nonabsorbing solvent, this is a familiar function defined as

$$E_m = \frac{1}{c \cdot l} \log \frac{I_0}{I} \quad , \tag{i}$$

where c is the concentration of the solute in moles per liter of solution, l the length of the light path in the solution in centimeters and $\log \frac{I_0}{I}$ the optical density.

For a pure absorbing liquid, or an absorbing liquid diluted with a non-absorbing solute, E_m is better defined by (ii)

$$E_m = \frac{M}{c \cdot l} \log \frac{I_0}{I} \, , \tag{ii}$$

where M is the molecular weight of the absorbing constituent and c is the concentration of the absorbing constituent in grams per liter of solution.

In Figs. 2, 6, 7, and 11, E_m is calculated in terms of the absorbing solvent (nitric acid) by Equation (ii). Table II and Fig. 9 deal with systems for which (i) is satisfactory. For the systems nitric acid – ammonium nitrate, and nitric acid – potassium nitrate, where "nitrate" is contributed by both the constituents of the solution, the curves are calculated in terms of the total nitrate ($E_{(NO_3)}$).

In Fig. 10 which is concerned with the spectrum of the equilibrium system between anhydrous nitric acid and nitrogen pentoxide no molar extinction coefficient has been calculated and the intensity data are left in terms of arbitrary density units, corrected only for the change in the specific gravity of the solutions which occurs on the addition of nitrogen pentoxide.

Determination of the Specific Gravity of the Solutions

The various solutions containing anhydrous nitric acid were prepared by the use of weight pipettes, from which the gravimetric concentrations of the solutions are obtained. In order to derive the molecular extinction

* *Subsequent to the completion of these investigations the existence of the stable nitronium (NO_2^+) ion has been established by Ingold and coworkers (14, 30).*

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coefficients from these measurements it was necessary to know the molar concentration, which involved the determination of the specific gravities of the solutions. Such measurements of specific gravity have been carried out on the following systems:—

Nitric acid – ammonium nitrate
Nitric acid – potassium nitrate
Nitric acid – ammonium acetate
Nitric acid – acetic acid.

The results are given in Table VI and in Fig. 12.

TABLE VI

DENSITIES OF ANHYDROUS NITRIC ACID SOLUTIONS

% NH_4NO_3	D_4^{20}	% KNO_3	D_4^{20}	% NH_4OAc	D_4^{20}	% HOAc	D_4^{20}	% N_2O_5	D_4^{25}*
0.00	1.513	—	—	—	—	—	—	0.0	1.501
5.01	1.527	9.98	1.582	5.02	1.508	12.70	1.441	6.0	1.530
10.81	1.548	14.97	1.621	9.84	1.501	28.40	1.361	12.0	1.560
19.72	1.568	19.99	1.658	14.95	1.491	37.17	1.322	18.0	1.588
26.75	1.579	25.00	1.695	20.60	1.478	49.40	1.265	24.0	1.618
54.00	1.578	—	—	25.00	1.459	66.37	1.186	30.0	1.645
—	—	—	—	29.90	1.440	79.70	1.131	—	—

* *Data supplied by Dr. E. G. Taylor*

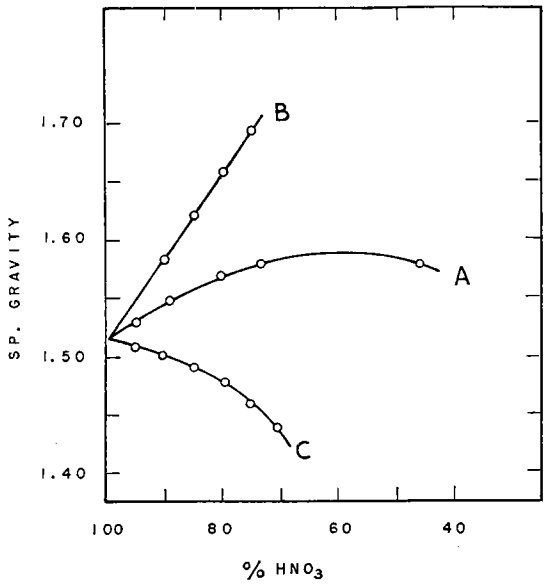

FIG. 12. *Specific gravities* ($d_{4^\circ}^{20^\circ}$).
A. Nitric acid – ammonium nitrate.
B. Nitric acid – potassium nitrate.
C. Nitric acid – ammonium acetate.

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The values for the specific gravity of aqueous solutions of nitric acid were taken from the International Critical Tables, and for solutions of nitrogen pentoxide in nitric acid from measurements made by Dr. Taylor in this laboratory. Approximate values for nitrogen pentoxide in acetic anhydride and in carbon tetrachloride were obtained by interpolation between the specific gravity values of solid nitrogen pentoxide (2.0), acetic anhydride (1.08), and carbon tetrachloride (1.59), assuming a linear variation with concentration. The data in Table VI represent the mean of duplicate determinations based on comparison of the weight of 10 ml. of solution with 10 ml. of water, using a volumetric flask as a pyknometer. Measurements were made at $20.0 \pm 0.1°$ C., and a correction for buoyancy applied. The precision in most cases is better than 0.001, and in no case was a variation greater than 0.002 observed.

Spectrographic Manipulation

A Beckman model DU ultraviolet spectrophotometer was used for the determination of the spectra. The majority of the solutions possessed too great an optical density to permit use of the standard 1 cm. cells. Cells were designed as shown in Fig. 13. They consisted of optically plane quartz disks

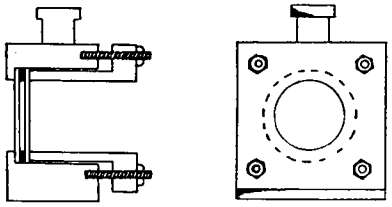

FIG. 13. *Thin cell for corrosive solutions.*

separated by platinum annuli and held in place in an aluminum holder. The quartz disks were 1 mm. thick and 26 mm. in diameter. The annuli were stamped from platinum sheet of 0.012, 0.1, and 1 mm. thickness. Aluminum and platinum were used as the metals most suitable to withstand the action of concentrated nitric acid (47).

A specially designed compartment containing a sliding carriage to hold two of these cells was placed between the main case of the spectrograph and the photocell compartment. Two quartz windows permitted entrance and exit of the monochromatic light beam through this compartment, and provision was made for the aspiration of a stream of air through the compartment to remove any corrosive fumes from the neighborhood of the spectrophotometer.

The cells were calibrated photometrically using potassium chromate (20, 29). The potassium chromate was recrystallized four times from 0.005 N potassium hydroxide and dried by pumping at 10^{-5} mm. for five hours. Several determinations of the optical density of standard chromate solutions

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were made for each cell. Using the value of E_{max} given by Hogness *et al.* (29) the cell thickness (l) was calculated from Equation (1).*

Two methods were employed in filling these cells. In the first method, which could be employed only for nonhygroscopic and nonvolatile material, the annulus and one quartz disk were placed on the inner section of the aluminum holder. A few drops of the liquid were then placed on the quartz disk. The second quartz disk was then lowered on to the annulus, after which the outer section of the holder was slipped over the inner section and tightened (Fig. 14*a*).

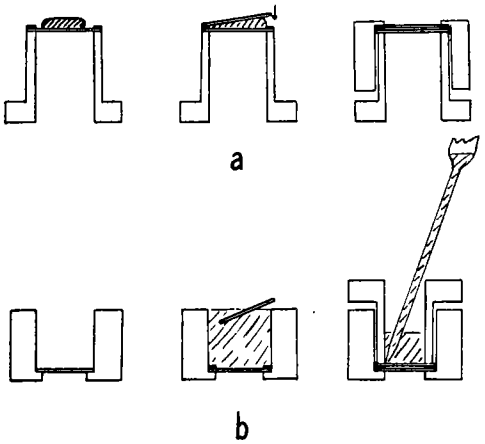

FIG. 14. *Diagrammatic illustration of technique for filling thin cell.*
a. For nonhygroscopic solutions.
b. For hygroscopic solutions.

The second method was used for hygroscopic acids. The outer section of the aluminum holder was placed in a shallow crystallizing dish, and one quartz disk lowered into place. The cavity of the cell holder was filled with the acid solution and the annulus and second quartz disk then slid into the solution and pushed down into place with a glass rod. The inner section of the holder was inserted, the excess acid removed with a pipette, and the whole tightened. Using this method of filling, the portion of solution which is confined between the quartz disks is never exposed to the air in a thin film (see Fig. 14*b*).

Reagents and Materials

Ammonium nitrate and ammonium acetate—Merck Reagent grade.

Potassium nitrate—"Analar" Reagent.

The ammonium nitrate and potassium nitrate were found to contain less than 0.1% moisture and were therefore used without further treatment.

* *In these calculations it is assumed that Beer's law holds accurately for solutions of potassium chromate over the concentrations used. The validity of this assumption is demonstrated by the agreement in the values of the molecular extinction coefficients for ammonium nitrate solutions (Table II) obtained with the same solution in cells of different thickness, since these cell thicknesses are based on measurements of the potassium chromate solutions as described above.*

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The ammonium acetate was pumped at 1 mm. pressure for several hours and used directly after pumping.

The nitric acid was prepared in an all-glass still. A mixture of two parts by volume of 96% sulphuric acid and one part of 70% nitric acid was distilled at a pressure of 30 mm. of mercury at 60° to 70°. A water-white product was obtained of 99.5 to 100.5% nitric acid content, which gave no test for chloride or sulphate ion. Solutions of lower concentration were prepared by diluting 40 or 50 gm. of the anhydrous acid with the calculated weight of water. The final concentration was determined by titrating a diluted sample with 0.2 *N* sodium hydroxide using phenolphthalein as indicator.

The acetic acid, acetic anhydride, and nitric acid – nitrogen pentoxide mixtures were prepared by Dr. E. G. Taylor and Dr. A. G. Follows in connection with investigations of electric conductivity carried out simultaneously with these spectrographic measurements. The acetic acid was obtained by careful fractionation of Reagent grade glacial acetic acid, the purity being checked by freezing point determinations. The acetic anhydride was distilled from calcium carbide and then fractionally redistilled. Nitrogen pentoxide was prepared by distillation of equal parts by weight of phosphorus pentoxide and anhydrous nitric acid at reduced pressure.

Acknowledgments

During the course of these investigations we had many fruitful discussions with Dr. E. G. Taylor, whose studies of the electrical conductivities and phase diagrams of certain of these systems will be published separately. Our thanks are also due to Dr. A. G. Follows and Mr. M. Lyne for supplies of anhydrous nitric acid and nitrogen pentoxide.

References

1. BALY, E. C. C., BURKE, K. A., and MARSDEN, E. G. J. Chem. Soc. 95 : 1096. 1909.
2. BAUER, E. and MAGAT, M. Cahiers phys. 5 : 37. 1941; *Abstracted in* Chem. Abstracts, 40 : 1734. 1946.
3. BAUER, E., MAGAT, M., and DE SILVEIRA, A. Compt. rend. 197 : 313. 1933.
4. BENNETT, G. M., BRAND, J. C. D., and WILLIAMS, G. J. Chem. Soc. 869. 1946.
5. BENNETT, G. M., BRAND, J. C. D., and WILLIAMS, G. J. Chem. Soc. 875. 1946.
6. BRINER, E., SUSZ, B., and FAVARGER, P. Helv. Chem. Acta, 18 : 375. 1935.
7. BRUNETTI, R. and OLLANO, Z. Nuovo cimentô, 6 : 522. 1930.
8. BRUNETTI, R. and OLLANO, Z. Nuovo cimento, 8 : 169. 1931.
9. CHÉDIN, J. Ann. chim. (Série 2) 8 : 243. 1937.
10. DANIELS, F. J. Am. Chem. Soc. 47 : 2856. 1925.
11. DALMON, R. Compt. rend. 207 : 473. 1938.
12. DALMON, R. and BELLIN, G. Compt. rend. 215 : 136. 1942.
13. DALMON, R. and FREYMAN, R. Compt. rend. 211 : 472. 1940.
14. GILLESPIE, R. J., GRAHAM, J., HUGHES, E. D., INGOLD, C. K., and PEELINGS, E. R. A. Nature, 158 : 480. 1946.
15. GRASSMAN, P. Naturwissenschaften, 20 : 560. 1932.
16. VON HALBAN, H. Z. physik. Chem. 120 : 268. 1926. *See also* Trans. Faraday Soc. 21 : 620. 1926.
17. VON HALBAN, H. Z. Electrochem. 34 : 489. 1928.

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18. VON HALBAN, H. and EISENBRAND, J. Z. physik. Chem. 132 : 401. 1928.
19. VON HALBAN, H. and EISENBRAND, J. Z physik Chem. 132 : 433. 1928.
20. VON HALBAN, H. and SIEDENTOPF, K. Z. physik. Chem. 100 : 208. 1922.
21. HANTZSCH, A. Ber. 58 : 941. 1925.
22. HANTZSCH, A. Z. physik. Chem. 149 : 161. 1930.
23. HANTZSCH, A. and BERGER, K. Ber. 61 : 1328. 1928.
24. HANTZSCH, A. and SCHARF, E. Ber. 46 : 3570. 1913.
25. HARTLEY, W. N. J. Chem. Soc. 81 : 556. 1902.
26. HARTLEY, W. N. J. Chem. Soc. 83 : 221. 1903.
27. HETTNER, G., POHLMAN, R., and SCHUMACHER, H. J. Naturwissenschaften, 21 : 884. 1933.
28. HIBBEN, J. H. The Raman effect and its chemical applications. Reinhold Publishing Corporation, New York. 1939.
29. HOGNESS, T. R., ZSCHEILE, F. P., and SIDWELL, A. E. J. Phys. Chem. 41 : 379. 1937.
30. INGOLD, C. K., MILLEN, D. J., and POOLE, H. G. Nature, 158 : 481. 1946.
31. JONES, R. N., THORN, G. D., LYNE, M., and TAYLOR, E. G. Nature, 159 : 163. 1947.
32. KINSEY, E. L. and ELLIS, J. W. Phys. Rev. 36 : 603. 1930.
33. KORTÜM, G. Z. physik. Chem. B, 43 : 418. 1939.
34. LEY, H. and ARENDS, B. Z. physik. Chem. B, 17 : 177. 1932.
35. MÉDARD, L. and PETITPAS, T. Compt. rend. 197 : 1221. 1933.
36. MÉDARD, L. and PETITPAS, T. Compt. rend. 198 : 88. 1934.
37. MORTON, R. A. and RIDING, R. W. Proc. Roy. Soc. (London), A, 113 : 717. 1926.
38. OLLANO, Z. Nuovo cimento, 9 : 264. 1932.
39. OLLANO, Z. and FRONGIA, G. Nuovo cimento, 10 : 306. 1933.
40. RAO, I. R. Proc. Roy. Soc. (London), A, 127 : 279. 1930.
41. SCHAEFER, K. Z. Electrochem. 21 : 181. 1915.
42. SCHAEFER, K. Z. anorg. u. allgem. Chem. 97 : 285. 1916.
43. SCHAEFER, K. Z. anorg. u. allgem. Chem. 98 : 77. 1916.
44. SCHEIBE, G. Ber. 59 : 1321. 1926.
45. DE SILVEIRA, A. Compt. rend. 197 : 1035. 1933.
46. TAYLOR, E. G. Private communication.
47. THOMPSON, J. G. Chem. and Met. Eng. 33 : 614. 1926.
48. VELEY, V. H. and MANLEY, J. J. J. Chem. Soc. 83 : 1015. 1903.

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